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Review on eco-friendly natural dyeing, different types of chemical bonds and its role in dyeing

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Abstract:-

Colour is a very important property of materials around us but we often neglect its study socially and scientifically. We perceive colour just as we perceive things like taste, smell, and touch etc. colour can influence our emotions, actions and how we respond to various things, people and ideas. Colour is extremely versatile in its uses. It can be used to make a statement, create an atmosphere, or call forth a response. Colour expresses outwards towards the world, but it also helps us to travel inwards towards spiritual states, towards our true self. This review paper reports the studies of natural dyestuff and its classification on the basis of hues, origin, chemical structure and method of application, extraction method of colorants ; effects of different mordants and mordanting methods; Natural Dyeing and mordants effect on fabrics with functionality, techniques of dyeing, adsorption process of dye ,different chemical bonds and its role in dyeing, fastness of textile dye, colour measurement, environmental concerns, advantages and disadvantages etc.

Keywords:- Dye, Mordant, ,Extraction Method, Technique Of Dyeing, Chemical Bonds, Fastness ,Colour Measurement.

1. Introduction

A dye is a coloured compound, normally used in solution, which is capable of being fixed to a fabric. The dye must be 'fast' or chemically stable so that the colour will not wash with soap and water, fade on exposure to sunlight etc. Dyeing is normally done in a special solution containing dyes and particular chemical material. After dyeing, dye molecules have uncut Chemical bond with fiber molecules. The temperature and time controlling are two key factors in dyeing.

a) **Dye:-**"It is defined as the compound which containing chromophore and auxochrome groups called dye. Chomophore group is responsible for dye colour due to their saturation. Auxochrome group is responsible for dye fibre reaction."
b) **Natural dye:-**Natural dyes are simply dye substances extracted from natural sources. Although the main source of dyes for early times, they have largely been replaced by synthetic dyes, which are usually more reliable, cheaper and can be supplied more readily. Natural dyes still in use include haematoxylin, carmine, orcein. Colouring materials have been used for many thousands of years by man. Leather, cloth, food, pottery and housing have all been modified in this way. Some of our most common dyes are still derived from natural sources. These are termed natural dyes. The Colour Index uses this as a classification and naming system. Natural dyes are often negatively charged. Positively charged natural dyes do exist, but are not common. In other words, the coloured part of the molecule is usually the anion. Although the molecular charge is often shown on a specific atom in structural formulae, it is the whole molecule that is charged. Many, but by no means all, natural dyes require the use of a mordant.

2. Classification of natural dyes

Natural dyes can be classified as:

a) On the basis of hues

- Red colour dyes: Red colour dyes are mostly produced from the roots and barks of plants and from the grey insects camouflaged. These dyes contain anthraquinone and its derivatives. These dyes have excellent wash and light fastness properties.
- Yellow colour dyes: Yellow colour most abundant hue in nature. Typically, they produce pale shade with more rapidly fading in contrasts, turmeric produces deep shades but poor fastness to light. Basically natural yellow dyes wash fastness lie between fair to excellent, e.g., turmeric, tesu, kapila.
- Blue colour dyes gives excellent fastness to washing and light, i.e. woad and indigo.
- Black colour dyes: Tannin rich plant produces black shades and having substantivity towards protein and cellulosic fibres provide good fastness properties, i.e. harda, logwood, custard apple etc .

b) On the basis of origin: generally natural dyes are obtained from mineral, vegetable and animal origin. Affluently 90% natural dyes are obtained from vegetable sources and the colouring matter extracted from flower, root, leaf, bark, and fruit of plants. For example,

- Root - turmeric, madder, onions etc.
- Bark - Purple bark, Shillicorai, Sappan wood, Red, Khair, Sandalwood
- Leaf- Indigo, Eucalyptus, Henna, Tea, Coral Jasmine, Cardamon, Lemon Grass
- Flower- Marigold, Dahlia, Tesu, Kusum
- Fruit- Pomegranate rind, Latkan, Beetle nut, Myrobolan (Harda) etc.

c) On the basis of Chemical Structures

- Indigoid dyes: Natural dyes acquired from Indigofera tinctoria.
- Anthraquinone dyes: Anthraquinone structure provides red colour dyes and basically procured from insects and plants. These dyes make complexes with metal salts and provide excellent fastness properties.
- Alpha-hydroxy-napthoquinones: The most well-known member of this group of dyes is henna, procured from Lawsonia inermis.
- Fla'Vones: Most of the natural yellow colours are hydroxy and methoxy derivatives of flavones and isoflavones.
- Dihydropyrans: Closely associated with flavones in chemical structure, are substitute of dihydropyrans.
- Anthocyananidins: procured from Bignonia chica.
- Carotenoids: The colour is caused by the presence of conjugated double bond, i.e. annatto and saffron.[91]

d) **On the basis of the method of application**

- Vat dyes- these are water insoluble dyes so first thing is to convert these dyes into water soluble for by reducing with Na- hydrosulphite and then solubilising it with alkali and then apply on the fibres. The accurate shade is formed simply on oxidation followed by cure with hot soap solution, e.g., indigo.
- Mordant dyes –these dyes don't have any affinity for fibres so mordants are used for dyeing. These dyes have electron donating groups so having ability of forming complex with the transition metal salt, e.g., fustic, madder, Persian, kermes, cochineal, berries etc.
- Direct dyes – for cellulosic fibres these dyes have strong affinity. They are dyed in boiling dye bath, i.e. harda, turmeric, pomegranate rind etc.
- Acid dyes-these are applied from an acidic medium. In acid dye molecules have either sulphonic or carboxylic group which form an electrovalent bond with amino groups of wool and silk. The fastness of these dyes improved by treteated with tannic acid e.g., saffron.
- Disperse dye- these dyes consists low solubility, low molecular mass, and no well-built solubilising groups and applied on to hydrophobic synthetic fibre in mild acidic pH , this is also apply on wool and silk fabrics. These dyes gives best fastness result on post mordanting with tin, chromium and copper salts e.g., anthroquinone and lawsone dyes.
- Basic or cationic dyes-these dyes make electrovalent bond with the carboxylic group of wool and silk and

gives coloured cations on ionization. These dye have poor light fastness and applied in mild acidic medium, e.g., berberine.

3 Extraction method of natural dyes

The extraction of natural dyes from plants, animals and minerals is depend on various substitute such as type of medium used (i.e. aqueous), pH of medium, condition of extraction such as temperature, time, material to liquor ratio and size of substrate .

a) **Aqueous extraction:-**The respective plant parts were taken and poured in boiling water and then kept on water bath at 60C for about one hour so as to extract the entire colour from them.
b) **Extraction by organic solvents:-** In this method organic solvents are used to extract the colour pigments from the respective plants parts. Various organic solvents are used for extraction of natural dyes, i.e. acetone, methanol, ethanol etc.
c) **Extraction by acid and alkali:-** The extraction of natural dye from the respective plants parts are done under acidic and alkaline condition by using HCl under acidic pH, sodium carbonate under alkaline pH .

4.Mordanting and methods of mordanting

A mordant is a substance used to set dyes on fabrics or tissue sections by forming a coordination complex with the dye which then attaches to the fabric or tissue. It may be used for dyeing fabrics, or for intensifying stains in cell or tissue preparations.

- Various mordants either chemical or natural mordants are used in dyeing of textiles.
- It is necessary that mordants have affinity both for fibre and dye particles.

a) Pre - Mordanting: - In this method the wool was first treated with mordant and then dyed under Optimized conditions.
b)Simultaneous -Mordanting:- In this method the wool was dyed with mordant at a same time under optimized conditions.
c) Post - Mordanting:- In case of postmordanting the fabric was first dyed under optimized conditions and then treated with mordant.

5. Techniques of Dyeing

a) Bale Dyeing: This is a low cost method to dye cotton cloth. The material is sent without scouring or singeing, through a cold water bath where the sized warp has affinity for the dye. Imitation chambray and comparable fabrics are often dyed this way.

b) Batik Dyeing: This is one of the oldest forms known to man. It originated in Java. Portions of the fabric are coated with wax so that only un-waxed areas will take on the dye matter. The operation may be repeated several times and several colors may use for the bizarre effects. Motifs show a mlange, mottled or streaked effect, imitated in machine printing.

c) Beam Dyeing: In this method the warp is dyed prior to weaving. It is wound onto a perforated beam and the dye is forced through the perforations thereby saturating the yarn with color.

d) Burl or speck Dyeing: This is done mostly on woolens or worsteds, colored specks and blemishes are covered by the use of special colored links which come in many colors and shades. It is a hand operation.

e) Chain Dyeing: This is used when yarns and cloth are low in tensile strength. Several cuts or pieces of cloth are tacked end-to-end and run through in a continuous chain in the dye color. This method affords high production.

f) Cross Dyeing: This is a very popular method in which varied color effects are obtained in the one dye bath for a cloth which contains fibers with varying affinities for the dye used. For example, a blue dyestuff might give nylon 6 a dark blue shade, nylon 6, 6 a light blue shade, and have no affinity for polyester area unscathed or white.

g) Jig Dyeing: This is done in a jig, kier, vat, beck or vessel in an open formation of the goods. The fabric goes from one roller to another through a deep dye bath until the desired shade is achieved.

h) Piece Dyeing: The dyeing of fabrics in the cut, bolt or piece form is called piece dyeing. It follows the weaving of the goods and provides a single color for the material, such as blue serge, a green organdy.

i) Random Dyeing: Coloring only certain designated portions of the yarn. There are three ways of doing this type of coloring: Skeins may be tightly dyed in two or more places and dyed at one side of the dye with one color and at the other side with another one. Color may be printed onto the skeins which are spread out on the blanket fabric of the printing machine.

6 Adsorption of Dye from the Dyebath

Several distinct and identifiable events take place in the dyeing of a textile material. The events are as follows:-

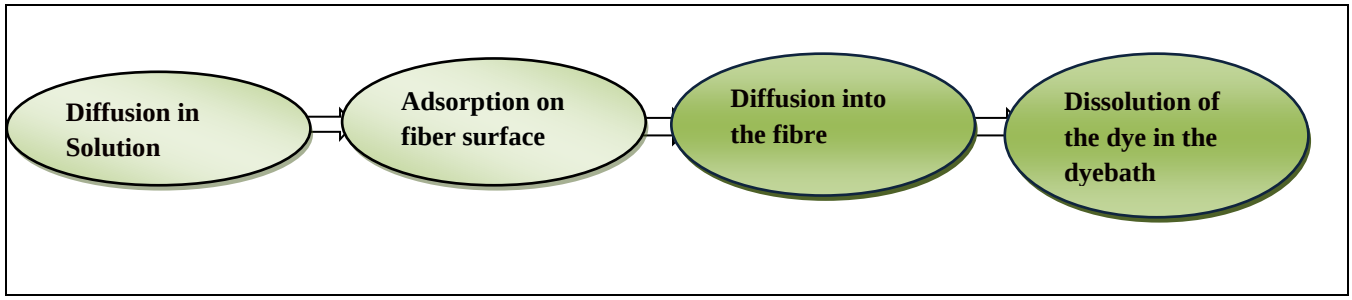

Table no 1 Adsorption of dye from dyebath on the fibre

a)Diffusion in Solution – Dye must move or diffuse through the dyebath in order to establish contact with the textile material being dyed.
b)Adsorption on fiber surface – dye molecules are attracted to the fibre and are initially deposited on the fibre surface.
c)Diffusion into the fibre – dye deposited on the surface creates a concentration gradient which is the driving force for movement of dye from the surface towards the interior of the fiber. During diffusion, dye molecules migrate from place to place on the fibre. This migration tends to have a levelling effect on the dye application. Dyes which migrate readily are easy to apply uniformaly. However, dyes which migrate and level easily also tends to have poorer wash fastness than dyes which do not level easily.
d)Dissolution of the dye in the dyebath – dyes which are only sparingly soluble in water may have to dissolve from a dispersion of highly aggregated particles in order to be small enough to diffuse into the fibre.

7.Different Types of Chemicals Bonds and its Role in Dyeing

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electromagnetic force attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. The reaction between dyes and fibres must take into account the various types of forces exerted by one molecule upon another. All **dyeing** mechanisms can be divided into following three groups:
1. Specific bond between dye and fibre owing to covalent bond, hydrogen bonds or other directed bonds.
2. Non- specific attraction between dye and fibre owing to ion-exchange or Van der Waals' forces.
3. Absence of any interaction, dyes is only mechanically retained. This may be due to insolubilisation of the dye inside the fibre or may be due to self –association into possibly quite large molecular aggregates following their entry into fibre. Aggregation is promoted by a high ratio of molecular weight to ionic group as well as by increase in

length of the aromatic structure of the molecule, also by rise in concentration and the presence of inorganic salts, e.g. common salt.

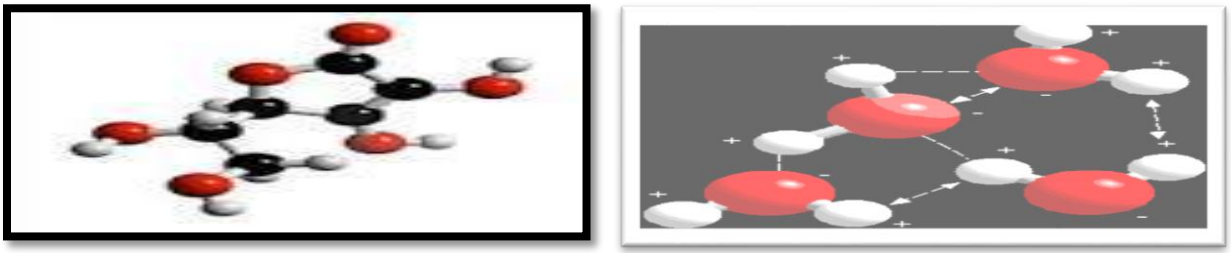

Figure no.1 a) Chemical bonds **b)negatively and positively charged chemical bonds**

a) **Vander Waal's Forces**

These forces are so named because they were first recognized by Van der Waals in 1873. Very weak forces of attraction are always present between the electrons of one atom and the nucleus of another in close enough proximity. Individually these are very weak forces, but collectively they are considered to be of sufficient strength to be the most important attractive forces between dye and fibre. These forces of attraction are known as Van der Waals' forces. Disperse dyes are held in a polyester fibre by means of Van der Waals' forces.

b) Hydrogen Bonds:

These forces of attraction are weak forces set up between certain atoms in the **dyestuff** molecule when they are close enough to other atoms in the fibre. One of these atoms is the hydrogen atom, hence the term "hydrogen bond". Some direct and vat dyes are "hydrogen bonded" in cellulose fibres.

c)Hydrophobic Bonding:

The hydrophobic groups, especially alkyl chains, tend to associate together and escape from aqueous environment. The effect due to two simultaneous causes-the Van der Waals' forces between the hydrogen groups and the hydrogen bonds between water molecules. Each set of forces causes respective assembly of molecules or groups to associate together and to exclude the other. Hydrophobic bonds occur when both the fibre and dye contain a considerable portion of purely hydrocarbon, aliphatic or aromatic, as with some dyes applied on wool or most dyes applied on polyester. It is strictly not a new type of bond or intermolecular force.

d)Salt Linkages or Ionic Bond:

These bonds play an important part in dyeing fibre containing amino groups, i.e. wool, silk and nylon with anionic dyes. In the presence of water or dilute acids the amino groups become protonated: -

$NH_2CH_2COOH \rightarrow NH_3^+CH_2COO^-$

Acid dyes, being anionic in solution, are attracted at the positive site of the fibre. As the fibre forms zwitterions on ionization, a negative charge is also created on the fibre. This negative charge is responsible for attraction towards basic dyes which forms cationic dye ions in solution. However, basic dyes are now mostly applied on acrylic fibres which contain strong acidic sites. Due to ionization in acidic medium, negative charged sites are created in fibre which attracts **cationic dye** ions.

e) Ion-Dipole Forces:

While attracting those of opposite charge, ions in solution can exert attraction upon any polar molecule, giving rise to so-called ion-dipole forces. These forces are largely responsible for aqueous solubility of dyes. The attraction between dipoles on the cellulose ether groups and ionic groups in the dye molecules is also proposed.

f)Covalent Bond:

Bonds resulting in very strong chemical forces that are not easy to break expect under serve conditions are called covalent bonds. The classic example is that of the combination of cellulose fibres with **reactive dyestuffs**, where the hydroxyl group in the cellulose is covalently bonded to a suitable atom in the reactive dye.

Fibre	Dye class having affinity	Types of dye-fibre bonds
Cellulosic: cotton, jute, rayon, etc.	Direct, vat, solublised vat and sulphur dye	Van der Waals' forces and hydrogen bonding
	Reactive dye	Covalent bonds
Polyester	Disperse dye	Van der Waals' forces and hydrogen bonding
Protein/polyamide: wool, silk, nylons	Direct, acid,metal complex and basic dye	Ionic bond or electrostatic bonds
	Reactive dye	Covalent bonds
Acrylic	Cationic	Ionic bond or electrostatic bonds
	Disperse dye	Van der Waals' forces and hydrogen bonding

Table no 2 Fibers, Dyes and Dye-Fiber Bonds

8. Fastness of Textile Dyes

Colour fastness is defined as the resistance of coloured materials to fading or running during processing or in subsequent useful life. The term is usually used in the context of clothes. The fading or colour running is brought about by Washing, rubbing, action of light, hot pressing and perspiration. Therefore, fastness tests include:washing fastness, rubbing fastness, light fastness, fastness to hot pressing and perspiration fastness.In the test, the material is treated with/under the influence of the agent under consideration for a specific time and the effect assessed using the grey scale for assessing change in colour. The extent of staining can also be assessed using the grey scale for assessing staining.

9. Colour Measurement

The colour of textile dyes is measured using the spectrophotometer. There are different spectrophotometers for different types of light e.g. Infrared spectrometer, ultraviolet- visible spectrometer etc. but the working principle is almost the same.

1) A white source such as the tungsten lamp usually provides the light for the spectrophotometer. The monochrometer is a prism, spectrum filter, or diffraction grating which spreads the light from the source into a spectrum. Although, the word "monochromatic" means one colour or one wavelength, the monochrometer and slit select a narrow band of light rather a single wavelength to be measured. The slit scans across the spectrum selecting the band of light to be measured. The monochrometer and slit may be placed either before the sample position giving the monochromatic illumination or after the sample position, giving polychromatic illumination.

However, only polychromatic illumination followed by separation the separation of the reflected light by a monochrometer gives an accurate spectrophotometric curve if the sample is fluorescent. The detector is a photoelectric device which converts the transmitted or reflected light to an electrical signal in a chart or computer records.

2) An abridged spectrophotometer measures a few narrow bands across the spectrum rather than scanning wavelength by wavelength. Typically about 16 bands each about 20 nm wide are measured. These instruments use series of filters to select the bands to be measured or may use a series of detectors to measure the reflectance at all of the wavelengths simultaneously. Abridged spectrophotometers are simpler and less expensive than scanning spectrophotometers, but provide less information.

10. Advantages and disadvantages of natural dyes

a) Advantages of natural dyes

- Natural dyes shades are typically soft, silky and calm to the individual's eye.

- Natural dyestuff can produce a wide range of colours by using different mordants.
- Natural dyestuffs produce extraordinary colour ideas and are automatically harmonizing.
- Natural dyes are easily available.
- In some dyeing process the waste becomes an ideal fertilizer i.e. Indigo, Harda etc. So, no problem of waste disposal.
- This is a labour demanding industry, so provide occupation opportunity for all those busy in farming, mining and these dyes used in textile/food/leather etc.
- Some of the natural dyes are improved with age, whilst man-made dyes lighten with time.
- Natural dyes are generally moth resistant and so used in kid's garments and food-stuffs for safety .

b) Disadvantages of natural dyes

- The colouring matter extracted from nature has low colour values and take more time for dyeing.
- The cost of dyeing with natural dyes considerably higher than with synthetic dyes.
- In case of sappan wood, the colourant convert from brasiline to brasilein causing colour change take place red to brown when treated in prolonged exposure to air.
- Even toxic mordants are used to improve the fastness properties of natural dyes .

11.Environmental Concerns :-

The natural dyeing should be carried out with the optimum recipes using as less chemical as possible during the dyeing process to reduce the pollutant produced and the harmful effect to the environment. Moreover, the dyestuffs that extracted without chemical used could act as fertiliser after composting in order to reduce the wastage produced and produce an organic fertilizer

12. Conclusion:-

At last said that dye is very important for Textile sector, because the fabrics are to make attractive to us by dyeing. Natural dyes cannot be used as simple alternatives to synthetic dyes and pigments. Natural dye have been providing different colour shade range and every colour have their different wavelength ,on the basis of different wavelength ,different shade of colour range are classified and that's are using for different purpose for eg. red is using for dangerous and white is for peace ,etc. Different extraction method have been following for getting colorants from colorants substances , each method of extraction have their different level of performance, its depend on types of solvent using and their extraction activity with substance of dye. Three mordanting methods(pre, meta and post) have been following for getting different shade of colour it also depend on the type of mordant using it can be natural and chemical mordants. Many different techniques of applying of dyeing on fabric have their different adsorption level and provide different shade of colour. Different types of chemical bond formation during applying of dyeing on to fabric ,that's have their different performance level from low to strong ,its depend on the type of dye molecule and fabric molecules that's contain negative and positive charge ,due to these charge bond formation is there and showing different level of performance from excellent to poor . They do, however, have the potential for application, in specified areas, to reduce the consumption of some of the more highly polluting synthetic dyes. They also have the potential to replace some of the toxic, sensitizing and carcinogenic dyes and intermediates. It has been found that natural dyes are used in antibacterial, deodorizing, UV-protection and also food products. So, natural dye have been provided many advantages for textile sector and it useful for human being at different level desired.

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